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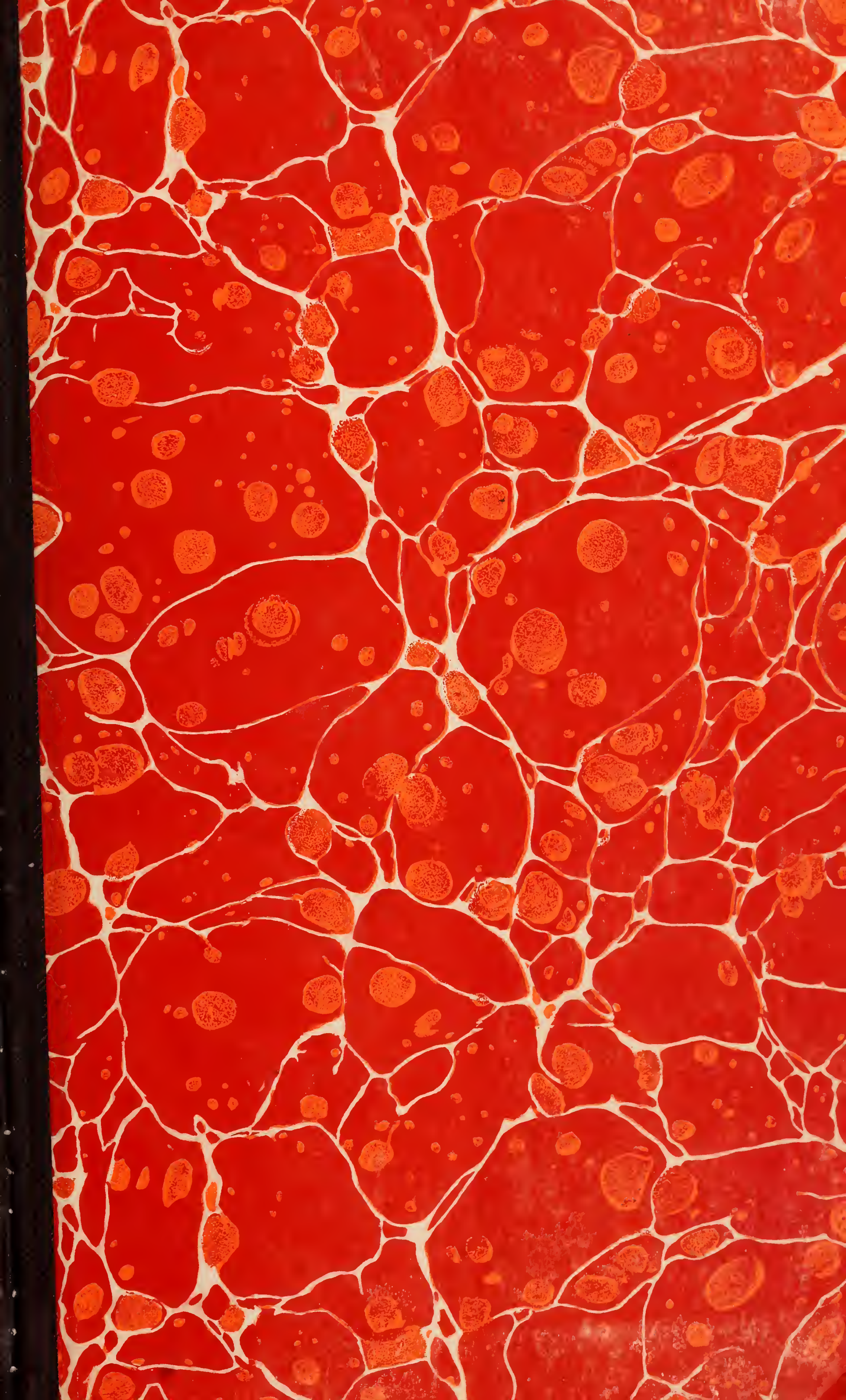

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RP309

THE HEAT OF IONIZATION OF WATER

By Frederick D. Rossini

ABSTRACT

The heat of ionization of water has been calculated by combining the data on heats of neutralization given by Richards and Rowe and the data on heats of dilution recently compiled by the present author. The value so obtained is corroborated by using the data on heats of neutralization reported by Gillespie, Lambert, and Gibson. For the reaction, $H_2O = H^+ + OH^-$, at infinite dilution in water and for the temperature range 10 to 35° C., the heat absorbed is given by the equation: $\Delta H = 13{,}721 - 57.9\ (t-18) + 0.15(t-18)^2$ g-cal$_{18}$ per mole. The uncertainty is estimated to be ±16 calories per mole. Using the factor 4.181 for coverting g-cal$_{18}$ to absolute joules gives $\Delta H = 57{,}370$ absolute joules per mole at 18° C.

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I. INTRODUCTION

The ionization of water may be expressed by the equation

$$H_2O = H^+ + OH^- \tag{1}$$

Although the heat absorbed in this reaction is not susceptible of direct measurement, its value can be determined in several ways.

Data on the change with temperature of the equilibrium constant for reaction (1) permits calculation of the change in heat content by means of the thermodynamic formula:[1]

$$\frac{d\ ln\ K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{R} \tag{2}$$

This method was employed by Noyes, Kato and Sosman,[2] who measured at various temperatures the hydrolysis of ammonium acetate and calculated the ionization constant for water.

A summation of the heat changes associated with appropriate other reactions may lead to the desired heat value. The following reactions compose such a series:

$$HCl{\cdot}100H_2O + NaOH{\cdot}100H_2O = NaCl{\cdot}201H_2O \tag{3}$$

$$HCl{\cdot}\infty H_2O = HCl{\cdot}100H_2O + (\infty - 100)H_2O \tag{4}$$

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[1] The nomenclature of Lewis and Randall ("Thermodynamics," McGraw-Hill Co., New York, 1923) will be used throughout this discussion.

[2] Noyes, Kato, and Sosman, J. Am. Chem. Soc., **32**, p. 159; 1910.

$$\mathrm{NaOH}\cdot\infty\mathrm{H_2O}=\mathrm{NaOH}\cdot 100\mathrm{H_2O}+(\infty-100)\mathrm{H_2O} \tag{5}$$

$$\mathrm{NaCl}\cdot 201\mathrm{H_2O}+(\infty-201)\mathrm{H_2O}=\mathrm{NaCl}\cdot\infty\mathrm{H_2O} \tag{6}$$

$$\mathrm{HCl}\cdot\infty\mathrm{H_2O}+\mathrm{NaOH}\cdot\infty\mathrm{H_2O}+\infty\mathrm{H_2O}=\mathrm{NaCl}\cdot\infty\mathrm{H_2O}+(2\infty+1)\mathrm{H_2O} \tag{7}$$

$$(\mathrm{H^+}+\mathrm{Cl^-}+\mathrm{Na^+}+\mathrm{OH^-})\cdot 3\infty\mathrm{H_2O}=(\mathrm{Na^+}+\mathrm{Cl^-}+\mathrm{H_2O})\cdot 3\infty\mathrm{H_2O} \tag{8}$$

or

$$\mathrm{H^+}+\mathrm{OH^-}=\mathrm{H_2O} \tag{9}$$

The reaction expressed by equation (7) is obtained by summing equations (3), (4), (5), and (6). Neglecting the somewhat philosophical question as to the heat of mixing $\mathrm{NaCl}\cdot\infty\mathrm{H_2O}$ with $2\infty\mathrm{H_2O}$, etc., which is negligibly small, equation (8) is equivalent to (7) and leads directly to the desired reaction (9). In other words, the heat of neutralization at infinite dilution may be taken as equivalent to the heat evolved when $\mathrm{H^+}$ combines with $\mathrm{OH^-}$ to form $\mathrm{H_2O}$, which reaction is the reverse of the ionization of water.

Utilizing the then best available data for the heat changes associated with reactions (3), (4), (5), and (6), Richards and Hall [3] calculated a value for the heat of ionization of water in the above manner. Richards and Rowe[4] obtained values for the heat of ionization of water by plotting heats of neutralization against the concentration and extrapolating the curves to infinite dilution. Richards and Mair [5] employed a like procedure.

In their calculation of the heat of ionization of water, Richards and Hall were limited to the use of one series of reactions because of the lack of suitable data on heats of dilution for electrolytes other than HCl, NaOH, and NaCl. Since that time, however, additional data on the heats of dilution of electrolytes in aqueous solution have been published, which permits the use of six different series of reactions.

It is the purpose of this paper to combine the data on heats of neutralization obtained by Richards and Rowe,[6] and incidentally the data of Gillespie, Lambert, and Gibson,[7] with the values for heats of dilution recently calculated by the present author,[8] and obtain a value for the heat of ionization of water by utilizing six different series of reactions similar to the one employed by Richards and Hall.

II. THE AVAILABLE DATA

1. HEATS OF NEUTRALIZATION

A review of the data on the heats of neutralization of uni-univalent strong electrolytes indicates that the only reliable measurements—especially with regard to purity of materials, proper statement of concentrations, and recognition of the proper temperature of the reaction—are those of Richards and Rowe,[9] and some few by Gillespie, Lambert, and Gibson.[10]

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[3] Richards and Hall, J. Am. Chem. Soc., **51**, p. 736; 1929.
[4] Richards and Rowe, J. Am. Chem. Soc., **44**, p. 703; 1922.
[5] Richards and Mair, J. Am. Chem. Soc., **51**, p. 739; 1929.
[6] Richards and Rowe, J. Am. Chem. Soc., **44**, p. 684; 1922.
[7] Gillespie, Lambert, and Gibson, J. Am. Chem. Soc., **52**, p. 3806; 1930.
[8] Rossini, B. S. Jour. Research, **6**, p. 791; 1931.
[9] See footnote 6.
[10] See footnote 7.

Richards and Rowe measured the heats of neutralization of HCl, HBr, HI, and HNO_3 with LiOH, NaOH, and KOH, respectively. Lack of suitable data on heats of dilution precludes the use of their data on HBr and HI in the present calculations. For each salt formed, Richards and Rowe performed 6 to 11 experiments, some having an initial temperature of about 15.5° C. and the remainder 16.5° C. The temperature rise in each experiment was about 4° C. These authors used the heat capacities of the factors in calculating the heat capacity of their calorimeter system, and, consequently, obtained the heat of the reaction at the final temperature. The heats of neutralization given by Richards and Rowe were reduced to 20° C. from the average values for the experiments having final temperatures of about 19.5° and 20.5° C., respectively. The concentration of each acid and base was 1 mole in 100 moles of H_2O, and the salt solution formed was $MX \cdot 201H_2O$.

The heats of neutralization calculated by Richards and Rowe depend directly upon the accuracy of the values chosen by them for the heat capacities of aqueous solutions of HCl, HNO_3, LiOH, NaOH, and KOH. Because of the fact that in most cases the heat capacities of aqueous solutions of acids and bases are not known as accurately as are those of the corresponding salt solutions, the present author has recalculated the heats of neutralization from the experimental data of Richards and Rowe, using the heat capacities of the formed salt solutions and thus obtaining the heat of neutralization at the initial temperature. Inasmuch as the amount of excess alkali solutions used by Richards and Rowe was only about 1/1000 of the resulting salt solution this latter can be assumed to be the pure salt solution in computing the heat capacity, without an error greater than 1 or 2 in 100,000. An example of the method of calculation employed for the data of Richards and Rowe is given in Table 1.

TABLE 1.—*Sample calculation*

Data given by Richards and Rowe for experiment No. 13:
  610.22 g $HCl \cdot 100.06H_2O$ and 615.42 g $NaOH \cdot 100.19H_2O$.
  Heat capacity of calorimeter = 18.98 g-cal_{18} per °C.
  Initial temperature = 15.66° C.
  Final temperature = 19.50° C.
  Average temperature = 17.58° C.
  Corrected temperature rise = 3.841° C.
Calculations by the present author:
  Heat capacity of formed solution (1,225.64 g $NaCl \cdot 201H_2O$) at the average temperature, 17.58° C. = (1,225.64) (0.97908) = 1, 200.00 g-cal_{18} per °C.
  Total heat capacity = 1,218.98 g-cal_{18} per °C.
  Total heat evolved = (1,218.98) (3.841) = 4,682.1 g-cal_{18}.
  Number of moles of HCl = 0.33180.
  Heat evolved per mole of HCl = 14,111 g-cal_{18}.
This gives the heat of reaction at the initial temperature, 15.66° C.

In the case of NaCl, Richards and Rowe performed five experiments at an average initial temperature of 16.79° C. and four at an average initial temperature of 15.66° C. A value for 16.00° C. was interpolated from the two average values, and the small correction for differences in concentration was made. In like manner, the data for the other five salts were calculated. A summary of the data of Richards and Rowe for 52 experiments is given in Table 2.

The values used by the present author for the specific heats of the various salt solutions at 18° C. were computed from values for the apparent molal heat capacities of these solutes in water at 18° C.[11] These values, given in Table 3, are slightly different from those of Richards and Rowe.[12]

TABLE 2.—*Data on heats of neutralization*

[From the data of Richards and Rowe]

Reaction	Number of experiments performed	Temperature of reaction	Δ *H*, heat absorbed
		° *C.*	*g-cal*$_{18}$ *per mole*
$HCl\cdot 100\ H_2O + LiOH\cdot 100\ H_2O = LiCl\cdot 201\ H_2O$	6	16.00	−14,173
$HCl\cdot 100\ H_2O + NaOH\cdot 100\ H_2O = NaCl\cdot 201\ H_2O$	9	16.00	−14,099
$HCl\cdot 100\ H_2O + KOH\cdot 100\ H_2O = KCl\cdot 201\ H_2O$	7	16.00	−14,189
$HNO_3\cdot 100\ H_2O + LiOH\cdot 100\ H_2O = LiNO_3\cdot 201\ H_2O$	10	16.00	−14,024
$HNO_3\cdot 100\ H_2O + NaOH\cdot 100\ H_2O = NaNO_3\cdot 201\ H_2O$	11	16.00	−14,031
$HNO_3\cdot 100\ H_2O + KOH\cdot 100\ H_2O = KNO_3\cdot 201\ H_2O$	9	16.00	−14,271

TABLE 3.—*Heat capacities of salt solutions at 18° C.*

Solution	Heat capacity of solution
	g-cal$_{18}$ $g^{-1}\ ^\circ C.^{-1}$
$LiCl\cdot 201\ H_2O$	0.9842
$NaCl\cdot 201\ H_2O$	.9792
$KCl\cdot 201\ H_2O$	.9730
$LiNO\cdot 201\ H_2O$	.9807
$NaNO_3\cdot 201\ H_2O$	.9760
$KNO_3\cdot 201\ H_2O$	.9702

Gillespie, Lambert, and Gibson reported the results of eight experiments on the heat of neutralization of NaOH and HCl, and one for KOH and HCl. Their data, excluding two experiments at 50° C., are given in Table 4. The next to the last column gives the heat capacities of the salt solutions as computed from the values for the apparent molal heat capacities of these aqueous salt solutions.[11] These can be compared with the values actually used by Gillespie, Lambert, and Gibson. The last column gives the heat of neutralization for the given temperature and concentration as corrected by these new values for heat capacity.

TABLE 4.—*Data on heats of neutralization*

[From the data of Gillespie, Lambert, and Gibson]

Experiment No.	Solution formed	Temperature of reaction = initial temperature	Average temperature	Heat capacity of salt solution at average temperature	Δ*H*, heat absorbed	Calculations by present author	
						Heat capacity of salt solution at average temperature	Δ*H*, heat absorbed
		°*C.*	°*C.*	*g-cal*$_{20}$ $g^{-1}\ ^\circ C^{-1}$	*g-cal*$_{20}$ *per mole*	*g-cal*$_{18}$ $g^{-1}\ ^\circ C^{-1}$	*g-cal*$_{18}$ *per mole*
1	$NaCl\cdot 1080.7\ H_2O$	20.00	20.35	0.9961	−13,784	0.9954	−13,774
2	$NaCl\cdot 566.5\ H_2O$	20.00	20.68	.9924	−13,803	.9917	−13,793
3	$NaCl\cdot 1101.4\ H_2O$	24.99	25.33	.9957	−13,582	.9948	−13,570
4	$NaCl\cdot 568.8\ H_2O$	32.27	32.92	.9922	−13,211	.9909	−13,194
5	$NaCl\cdot 566.0\ H_2O$	32.27	32.95	.9922	−13,274	.9909	−13,257
6	$NaCl\cdot 520.5\ H_2O$	32.30	33.01	.9916	−13,284	.9902	−13,265
9	$KCl\cdot 547.8\ H_2O$	20.00	20.71	.9896	−13,864	.9893	−13,859

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[11] Rossini, B. S. Jour. Research; 1931.

[12] Richards and Rowe, J. Am. Chem. Soc., **41**, p. 770; 1921.

2. HEATS OF DILUTION

The changes in heat content associated with reactions (4), (5), and (6) can be obtained from the values of $\Phi_h - \Phi_h{}^\circ$, the relative apparent molal heat content of the solute, given for aqueous solutions of HCl, HNO_3, LiOH, NaOH, KOH, LiCl, NaCl, KCl, $LiNO_3$, $NaNO_3$, and KNO_3, at 18° C., by the present author in a previous publication.[13]

For example, in reaction (4)

$$HCl \cdot \infty H_2O = HCl \cdot 100\ H_2O + (\infty - 100)\ H_2O \qquad (4)$$

$$\Delta H = \Phi_h - \Phi_h{}^\circ \qquad (10)$$

where Φ_h is the apparent molal heat content of HCl in the solution $HCl \cdot 100\ H_2O$, and $\Phi_h{}^\circ$ is the apparent molal heat content of HCl at infinite dilution in water.

III. THE CALCULATED RESULTS

The values cited above for heats of dilution are given for 18° C.; the data of Richards and Rowe on heats of neutralization, shown in Table 2, are for 16° C.; and those of Gillespie, Lambert, and Gibson on heats of neutralization are given at temperatures of 20°, 25°, and 32.3° C. (Table 4.)

Because the changes in heat content for these reactions have large temperature coefficients, it is necessary that these latter be known accurately for the proper conversion of the various data to 18° C. Once the values for the heats of neutralization are calculated to 18° C., it becomes a relatively simple matter to sum the changes in heat content for reactions (3), (4), (5), and (6), and obtain thereby values for the change in heat content for reaction (9)

$$H^+ + OH^- = H_2O \qquad (9)$$

For reaction (3)

$$HCl \cdot 100\ H_2O + NaOH \cdot 100\ H_2O = NaCl \cdot 201\ H_2O \qquad (3)$$

the temperature coefficient of the change in heat content is given by

$$\Delta C_p = 201\ \overline{C}^\circ_{p1} + \Phi_{c(NaCl)} - (100\overline{C}^\circ_{p1} + \Phi_{c(HCl)} + 100\overline{C}^\circ_{p1} + \Phi_{c(NaOH)}) \qquad (11)$$

or

$$\Delta C_p = \overline{C}^\circ_{p1} + \Phi_{c(NaCl)} - \Phi_{c(HCl)} - \Phi_{c(NaOH)} \qquad (12)$$

where $\Phi_{c(NaCl)}$, $\Phi_{c(HCl)}$ and $\Phi_{c(NaOH)}$ are the apparent molal heat capacities of NaCl, HCl, and NaOH in their respective solutions and $\overline{C}^\circ_{p1}$ is the molal heat capacity of pure H_2O. In correcting a heat of neutralization from t° C. to 18° C., values of Φ_c for the average temperature, $\frac{t+18}{2}$ °C., are needed. For converting the data of Richards and Rowe from 16° to 18° C., values of Φ_c for 17° C. were used; and for converting the data of Gillespie, Lambert, and Gibson from 32.3°, 25°, and 20° to 18° C., values of Φ_c for 25°, 21.5°, and 19° C., respectively, were used.[14]

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[13] See footnote 8, p. 848.

A comparison of the temperature coefficients given by Richards and Rowe[15] for the six different heats of neutralization with those calculated by the present author is given in Table 5.

The data of Richards and Rowe on heats of neutralization at 16° C., as given in Table 3, can now be converted to 18° C., and combined with the appropriate heats of dilution, to give values for the heat of ionization of water. The results of these calculations are summarized in Table 6.

The calculations from the data of Gillespie, Lambert, and Gibson are summarized in Table 7.

TABLE 5.—*Temperature coefficient of heat of neutralization, at 18° C.*

[For the reaction: $HX \cdot 100\ H_2O + MOH \cdot 100\ H_2O = MX \cdot 201\ H_2O$]

Solution formed	ΔC_p, in cal. mole^{-1}°C.$^{-1}$	
	Richards and Rowe	Present author
$LiCl \cdot 201\ H_2O$	55. 4	42. 3
$NaCl \cdot 201\ H_2O$	52. 7	46. 0
$KCl \cdot 201\ H_2O$	48. 4	46. 4
$LiNO_3 \cdot 201\ H_2O$	53. 6	40. 8
$NaNO_3 \cdot 201\ H_2O$	50. 5	45. 7
$KNO_3 \cdot 201\ H_2O$	45. 1	47. 3

TABLE 6.—*The heat of neutralization at infinite dilution*

[Combining data of Richards and Rowe with data on heats of dilution.]

Solution formed	$HX \cdot 100\ H_2O + MOH \cdot 100\ H_2O = MX \cdot 201\ H_2O$			Heats of dilution at 18° C., g-cal.$_{18}$ per mole			$H^+ + OH^- = H_2O$	Deviation from mean
	ΔH at 16° C. g-cal.$_{18}$ per mole	ΔC_p at 17° C. g-cal.$_{18}$ mole^{-1}° C^{-1}	ΔH at 18° C. g-cal.$_{18}$ per mole	Acid $\Phi_h - \Phi_h{}^\circ$	Base $\Phi_h - \Phi_h{}^\circ$	Salt $\Phi_h{}^\circ - \Phi_h$	ΔH at 18°C. g-cal.$_{18}$ per mole	
$LiCl \cdot 201\ H_2O$	−14, 173	42. 6	−14, 088	+305	+243	−174	−13, 714	+7
$NaCl \cdot 201\ H_2O$	−14, 099	46. 3	−14, 006	+305	+39	−48	−13, 710	+11
$KCl \cdot 201\ H_2O$	−14, 189	46. 7	−14, 096	+305	+137	−46	−13, 700	+21
$LiNO_3 \cdot 201\ H_2O$	−14, 024	41. 1	−13, 942	+86	+243	−132	−13, 745	−24
$NaNO_3 \cdot 201\ H_2O$	−14, 031	46. 0	−13, 939	+86	+39	+83	−13, 731	−10
$KNO_3 \cdot 201\ H_2O$	−14, 271	47. 6	−14, 176	+86	+137	+229	−13, 724	−3
Mean							−13, 721	±13

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[14] See footnote 11, p. 850.

[15] Richards and Rowe, J. Am. Chem. Soc., **44**, p. 699; 1922.

TABLE 7.—*The heat of neutralization at infinite dilution*

[Combining data of Gillespie, Lambert, and Gibson with data on heats of dilution]

Solution formed	$HX \cdot nH_2O + MOH \cdot nH_2O = MX \cdot (2n+1)\ H_2O$				Heats of dilution at 18° C., g-cal.18 per mole			$H^+ + OH^- = H_2O$	Deviation from mean
	The reaction temperature. ° C.	ΔH at reaction temperature. g-cal.18 per mole	ΔC_p at $\left(\frac{t+18}{2}\right)^\circ$ C.g-cal.18 mole^{-1} °C.$^{-1}$	ΔH at 18° C. g-cal.18 per mole	Acid $\Phi_h - \Phi_h^\circ$	Base $\Phi_h - \Phi_h^\circ$	Salt $\Phi_h^\circ - \Phi_h$	ΔH at 18° C. g-cal.18 per mole	
$NaCl \cdot 1080.7H_2O$	20.00	−13,774	52.6	−13,879	+140	+84	−59	−13,714	+4
$NaCl \cdot 566.5H_2O$	20.00	−13,794	50.5	−13,895	+190	+85	−63	−13,683	+35
$NaCl \cdot 1101.4H_2O$	24.99	−13,568	51.8	−13,931	+139	+83	−58	−13,767	−49
$NaCl \cdot 568.8H_2O$	32.27	−13,192	48.8	−13,890	+190	+85	−63	−13,678	+40
$NaCl \cdot 566.0H_2O$	32.27	−13,253	48.8	−13,951	+190	+85	−63	−13,739	−21
$NaCl \cdot 521.0H_2O$	32.30	−13,263	48.6	−13,958	+197	+84	−63	−13,740	−22
$KCl \cdot 547.8H_2O$	20.00	−13,858	50.7	−13,959	+193	+123	−60	−13,703	+15
Mean								−13,718	±27

IV. THE TEMPERATURE COEFFICIENT

The temperature coefficient of the heat of reaction (9)

$$H^+ + OH^- = H_2O \tag{9}$$

can be calculated from the values of the heat capacities of the substances involved. That is

$$\Delta C_p = \overline{C}_r{}^\circ{}_{(H_2O)} - \left(\overline{C}_p{}^\circ{}_{(H+)} + \overline{C}_p{}^\circ{}_{(OH-)}\right) \tag{13}$$

The heat capacity of H_2O is known, and the sum of the partial molal heat capacities[16] for H^+ and OH^- at infinite dilution can be determined as follows:

$\overline{C}_{p2}{}^\circ$, the partial molal heat capacity of the solute at infinite dilution, is known for NaCl, HCl, and NaOH. Now

$$\overline{C}_p{}^\circ{}_{(HCl)} + \overline{C}_p{}^\circ{}_{(NaOH)} = \overline{C}_p{}^\circ{}_{(H+)} + \overline{C}_p{}^\circ{}_{(Cl-)} + \overline{C}_p{}^\circ{}_{(Na+)} + \overline{C}_p{}^\circ{}_{(OH-)} \tag{14}$$

and

$$\overline{C}_p{}^\circ{}_{(NaCl)} = \overline{C}_p{}^\circ{}_{(Na+)} + \overline{C}_p{}^\circ{}_{(Cl-)} \tag{15}$$

Subtracting equation (15) from equation (14) gives

$$\overline{C}_p{}^\circ{}_{(HCl)} + \overline{C}_p{}^\circ{}_{(NaOH)} - \overline{C}_p{}^\circ{}_{(NaCl)} = \overline{C}_p{}^\circ{}_{(H+)} + \overline{C}_p{}^\circ{}_{(OH-)} \tag{16}$$

From the values for Φ°_c (which is equal to $\overline{C}_{p2}{}^\circ$) compiled by the present author,[17] one finds, for 18° C.,

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[16] For an extended discussion of apparent and partial molal heat capacities in aqueous solution see (a) Randall and Rossini, J. Am. Chem. Soc., **51**, p. 323; 1929; and (*b*) Rossini, B. S. Jour. Research, **4**, p. 313; 1930.

[17] See footnote 11, p. 850.

$$\overline{C}_p{}^\circ{}_{(\mathrm{H}^+)} + \overline{C}_p{}^\circ{}_{\mathrm{OH}^-} = -39.9 \text{ g-cal. mole}^{-1}\ {}^\circ C.^{-1} \qquad (17)$$

And for reaction (1)

$$\mathrm{H_2O} = \mathrm{H}^+ + \mathrm{OH}^- \qquad (1)$$

$$\Delta C_p = -39.9 - 18.0 = -57.9 \text{ g-cal. mole}^{-1}\ {}^\circ C.^{-1} \qquad (18)$$

The temperature coefficient[17] of $\overline{C}_p{}^\circ{}_{(\mathrm{H}^+)} + \overline{C}_p{}^\circ{}_{(\mathrm{OH}^-)}$ can be taken as 0.3 g-cal. mole^{-1} °C.$^{-2}$. For any temperature t, near 18° C., the temperature coefficient of the heat change associated with reaction (1) is

$$\Delta C_p = -57.9 + 0.3(t-18) \text{ g-cal. mole}^{-1}\ {}^\circ C.^{-1} \qquad (19)$$

V. DISCUSSION

The value for the change in heat content for reaction (9), as obtained from the data of Richards and Rowe on heats of neutralization, is

$$\Delta \mathrm{H} = -13{,}721 \qquad \text{g-cal.}_{18} \text{ per mole at } 18^\circ \text{ C.} \qquad (20)$$

or for the ionization reaction

$$\Delta \mathrm{H} = 13{,}721 \qquad \text{g-cal.}_{18} \text{ per mole at } 18^\circ \text{ C.} \qquad (21)$$

The average deviation of the six individual results from this value is ± 13 calories per mole.

Using the data of Gillespie, Lambert, and Gibson on heats of neutralization, one obtains for the ionization of water

$$\Delta \mathrm{H} = 13{,}718 \qquad \text{g-cal.}_{18} \text{ per mole at } 18^\circ \text{ C.} \qquad (22)$$

Here the average deviation is ±27 calories per mole. Inasmuch as the experiments of Gillespie, Lambert, and Gibson consist of 3 at 20° C., 1 at 25° C., and 3 at 32.3° C., as compared with the 52 experiments of Richards and Rowe at 16° C., the value given by equation (21) will be selected as the "best" value for the change in heat content which accompanies the ionization of water at infinite dilution. The value obtained from the Gillespie, Lambert, and Gibson data serves as an excellent verification of the selected value. The agreement also serves to establish the reliability of the heat content values [18] as well as the apparent molal heat capacity values[19] which were used to convert the data of Gillespie, Lambert, and Gibson to infinite dilution and to 18° C., respectively.

The error in the value calculated for the heat of ionization of water by the present method depends upon the accuracy of the determination of the various heats of neutralization and of the heats of dilution. The absolute accuracy of the final values for heats of neutralization calculated from the data of Richards and Rowe, using the new heat

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[18] See footnote 8, p. 848.

[19] See footnote 11, p. 850.

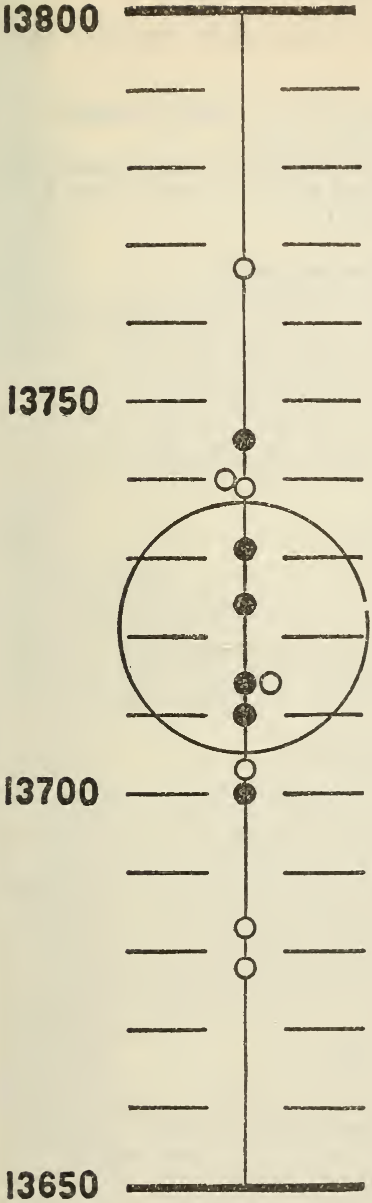

FIGURE 1.—*Plot of the data on the heat of ionization of water*

The ordinate scale, in g-cal.$_{18}$ per mole, gives the heat absorbed in the reaction, $H_2O = H^+ + OH^-$, at 18° C. and infinite dilution. The circle shows the estimated error in the selected "best" value, 13,721. The values obtained from the data of Richards and Rowe on heats of neutralization are indicated by ●; and those from the data of Gillespie, Lambert, and Gibson by ○. The latter values are from single experiments on the heat of neutralization, while the values of Richards and Rowe for heats of neutralization are each the average of 6 to 11 experimental values.

capacity values, can be placed at ± 8 calories per mole. If the uncertainty in the heats of dilution for reactions (4), (5), and (6) is estimated to be in each case ± 8 calories, the error in the final selected value for ΔH may be taken as $\pm\sqrt{8^2+8^2+8^2+8^2} = \pm 16$ calories per mole.

A graphical representation of the results obtained for the heat of ionization of water from the data of Richards and Rowe, and of Gillespie, Lambert, and Gibson, on heats of neutralization is shown in Figure 1.

It is interesting to note the values obtained for the heat of ionization of water by the investigators cited at the beginning of this paper.

For the ionization reaction

$$H_2O = H^+ + OH^- \qquad (1)$$

the values, converted by means of the proper temperature coefficient to 18° C., from whatever temperature they were given are:

ΔH, at 18° C., in g-cal.$_{18}$ per mole

Noyes, Kato, and Sosman	14,070.
Richards and Rowe	Between 13,730 and 13,790.
Richards and Hall	13,760.
Richards and Mair	13,760.
This paper	13,721.

VI. CONCLUSION

By combining the data on heats of neutralization obtained by Richards and Rowe with appropriate heats of dilution, there has been found for the reaction

$$H_2O = H^+ + OH^- \qquad (1)$$

$$\Delta H = 13{,}721 \pm 16 \text{ g-cal.}_{18} \text{ per mole at } 18° \text{ C.} \qquad (23)$$

and

$$\Delta C_P = -57.9 + 0.3(t-18) \text{ g-cal.}_{18} \text{ per mole per degree} \qquad (24)$$

For the temperature range of about 10° to 35° C., the heat absorbed in reaction (1), at infinite dilution in water, can be expressed by the equation

$$\Delta H = 13{,}721 - 57.9\ (t-18) + 0.15\ (t-18)^2 \qquad \text{g-cal.}_{18} \text{ per mole} \quad (25)$$

Here t is in °C. and the unit calorie is the actual heat capacity of 1 g of water at 18° C. Using the factor 4.181 for converting g-cal.$_{18}$ to absolute joules, gives, per mole at 18° C.,

$$\Delta H = 57{,}370 \text{ absolute joules} \qquad (26)$$

WASHINGTON, February 14, 1931.

7/13/54

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